CYCLEN PHOSPHORANES.   I. THE SYNTHESIS OF TETRAAMINOPHOSPHORANES -- A REMARKABLE
DEMONSTRATION OF A MACROCYCLIC EFFECT

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Schmutzler developed the synthesis of mono- and bis(dialkylamino)fluorophosphoranes from
fluorophosphoranes (e.g. PF_5) and silylated amines.[2]

$$R_2NSi(CH_3)_3 + PF_5 \xrightarrow{-78°} FSi(CH_3)_3 + R_2NPF_4 \xrightarrow[150°]{R_2NSi(CH_3)_3} (R_2N)_2PF_3$$
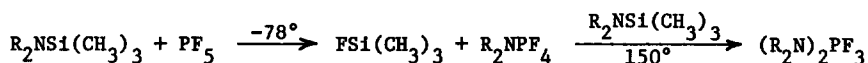
Displacement of the first fluorine of PF_5 is very rapid, but the second displacement is much
slower and the reaction stops at this stage.

We report an extension of this reaction to a macrocyclic system where the reaction pro-
ceeds to the displacement of four fluorines from PF_5. This reaction leads to a new class of
phosphoranes wherein phosphorus is bonded to four amino groups in a cyclic array.

The tetraazacyclododecane ligand 1, termed "cyclen,"[3] can be lithiated and silylated to
give tetrakis(trimethylsilyl)cyclen(2). In the presence of an equivalent of phosphorus

1   2, R = SiMe$_3$ 3
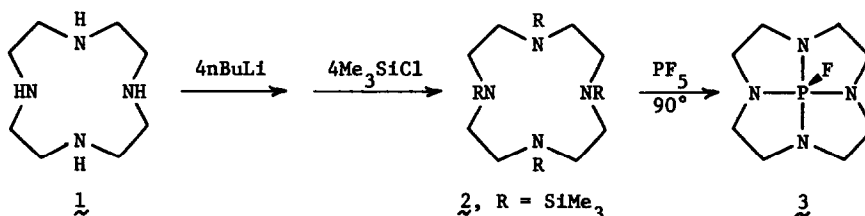
pentafluoride the silylated cyclen reacts smoothly at 90° to give cyclen fluorophosphorane(3),
in which all four silylated amines have displaced fluorine from PF_5. Four equivalents of tri-
methylsilylfluoride are produced. This is a remarkable demonstration of the unusual chemistry
observed in macrocyclic systems:[4] the reaction proceeds two additional steps and at a lower
temperature than does the acyclic analogue.

The less reactive substituted fluorophosphoranes 4a and 4b react with 2 at a higher temperature also proceeding to the fourth displacement. Cyclen phenylphosphorane(5a) and cyclen methylphosphorane(5b) are formed in good yield. We transgressed the limitations of the reaction in an attempted extension to pyrrolidyltetrafluorophosphorane(4c). In this case the low reactivity of the partially aminated intermediates from 4c is sufficient to stop the reaction at the second or possibly third displacement of fluorine (by nmr integration).

$$RPF_4 \ + \ 2 \longrightarrow$$

4   a, R = C_6H_5

     b, R = CH_3

     c, R = $N(C_4H_8)$

5   a, R = C_6H_5

     b, R = CH_3
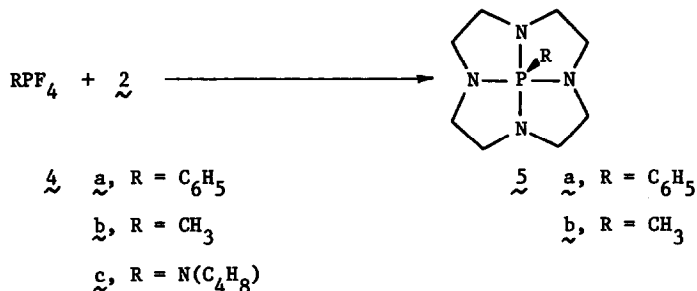
The structure of cyclen fluorophosphorane(3) was unequivocally established by x-ray crystallography.[5] The structure of 3 is essentially at the midpoint between the ideal square-pyramidal and trigonal-bipyramidal geometries for pentacoordinate phosphorus. If this structure is viewed as distorted trigonal bipyramid, then two nitrogens and fluorine occupy the pseudo-equitorial positions. When viewed as a distorted square pyramid, the fluorine occupies the pseudoapical position. Either interpretation places the more electronegative substituent (F) at the thermodynamically less favorable position.[6] The unusual intermediate geometry[7] of cyclen fluorophosphorane(3) is probably the result of the conformational requirements of the peripheral (12-membered) ring.

Each of the nitrogens in 3 is a flattened tetrahedral center. The average sum of the three angles at the pseudoequitorial nitrogens is 352° and at the pseudoaxial nitrogens is 347°. For ideal tetrahedral geometry the sum of angles is 328.5°. It is not clear whether this is the result of ring conformational requirements or electronic demands from the phosphorus. The nitrogens in acyclic aminophosphoranes are usually assumed to be planar.[8]

The proton nmr spectrum of 3 in $CDCl_3$ is a complex asymmetric multiplet; however, double decoupling of ^{31}P and ^{19}F reduces the spectrum to a symmetric AA'BB' pattern.[9] Cooling to −47° causes line broadening but the pattern remains symmetrical. This is consistent with rapid pseudorotation in 3 by a process that interconverts the two nitrogen (and carbon) positions. The sidedness of 3 requires that each of the equilibrated methylene groups maintains two

different proton environments resulting in an AA'BB' pattern for each of the identical ethylene groups.

The ^{31}P nmr spectrum of $\underset{\sim}{3}$ in benzene shows a doublet (J_{PF} = 799 Hz) 14.2 ppm upfield from phosphoric acid. The ^{19}F nmr in CDCl$_3$ also appears as a doublet (J_{PF} = 793 Hz) 75.4 ppm upfield from Freon-11. This coupling constant is intermediate between the equitorial (J_{PF} = 871 Hz) and axial (J_{PF} = 752 Hz) fluorines in [(CH$_3$)$_2$N]$_2$PF$_3$.[10]

The infrared, nmr,[9] and mass spectra of $\underset{\sim}{3}$, $\underset{\sim}{5a}$, and $\underset{\sim}{5b}$ have similarities that suggest a close resemblance in the structures of these cyclen phosphoranes. Further details of the spectroscopy and chemistry of these compounds will be reported in subsequent papers in this series.

EXPERIMENTAL

Tetrakis(trimethylsilyl)cyclen ($\underset{\sim}{2}$).[11] Cyclen[12] ($\underset{\sim}{1}$) slurried in dry tetrahydrofuran at −78° was treated with four molar equivalents of n-butyllithium/hexane. After stirring at 0° and recooling to −78°, the milky slurry was treated with four molar equivalents of trimethylchlorosilane. Warming, filtration and evaporation gave crystalline $\underset{\sim}{2}$ which was purified by recrystallization from petroleum ether and/or sublimation at 110°/0.1 mm, mp 140–150°.

Cyclen Fluorophosphorane ($\underset{\sim}{3}$). A frozen solution of 14.1 g (30.6 mmol) of $\underset{\sim}{2}$ in 100 ml of chlorobenzene was thawed under 770 ml of PF$_5$ gas. This mixture was slowly warmed and maintained 1 hr at 90°. Sublimation of the concentrate residue at 100°/0.1 mm gave 5.0 g (75%) of $\underset{\sim}{3}$, mp 87–92°. The crystals for x-ray determination were grown by careful sublimation and protected from moisture.

Cyclen Phenylphosphorane ($\underset{\sim}{5a}$).[11] A solution of 5.0 g (10.8 mmol) of $\underset{\sim}{2}$ and 2.0 g (10.8 mmol) of $\underset{\sim}{4a}$[13] in 50 ml of o-dichlorobenzene was heated 1 hr at 140–150°. A small drop of water was added to catalyze the reaction followed by heating at 130–160° for 20 hr. The solvent was distilled and the residue sublimed at 100°/0.02 mm giving 2.7 g (90%) of $\underset{\sim}{5a}$, mp 140–142°. NMR (^{31}P, C$_6$H$_6$): −45.3 ppm.

Cyclen Methylphosphorane ($\underset{\sim}{5b}$). A procedure similar to that for $\underset{\sim}{5a}$ gave 82% yield of $\underset{\sim}{5b}$, bp 120–140°/1.0 mm, mp 35°, from $\underset{\sim}{4b}$.

Atkins will be co-author of a subsequent paper in this series describing work that preceded this work.

REFERENCES AND FOOTNOTES

1. Present address: Department of Chemistry, University of Idaho, Moscow, Idaho 83843.

2. (a) R. Schmutzler, Angew. Chem. Internat. Edit., 3, 753 (1964); (b) ibid, 4, 496 (1965).

3. J. P. Collman and P. W. Schneider, Inorg. Chem., 5, 1380 (1966).

4. The term "macrocyclic effect" describes the enhanced stability of complexes of macrocyclic ligands compared to their acyclic counterparts. See for example F. P. Hinz and D. W. Margerum, Inorg. Chem., 13, 2941 (1974).

5. The x-ray determination was performed by R. C. Gearhart and L. J. Guggenberger. Details will be reported separately.

6. R. Hoffmann, J. M. Howell, and E. L. Muetterties, J. Amer. Chem. Soc., 94, 3047 (1972).

7. M. Eisenhut, R. Schmutzler and W. S. Sheldrick, J. C. S. Chem. Comm., 144 (1973) report an intermediate structure for a methyltetraarylthiophosphorane.

8. For conclusions derived from the photoelectron spectra of dimethylaminofluorophosphoranes see A. H. Cowley, M. J. S. Dewar, D. W. Goodman and J. R. Schweiger, J. Amer. Chem. Soc., 95, 6506 (1973).

9. The analysis of the nmr spectra of these and other cyclen phosphoranes was done by G. S. Reddy. This work will be reported independently.

10. D. H. Brown, G. W. Fraser, and D. W. A. Sharp, Chem. Ind. (London), 367 (1964).

11. C, H, N (and P) analyses were within 0.3% for this compound.

12. J. E. Richman and T. J. Atkins, J. Amer. Chem. Soc., 96, 2268 (1974).

13. R. Schmutzler, Chem. Ind. (London), 1868 (1962).